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MERCURY INVENTORY IN THE CACHE CREEK CANYON

Staff Report

February 2008

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EXECUTIVE SUMMARY

Methyl mercury is a developmental toxin for both humans and wildlife. The primary route of exposure is through consumption of fish. Advisories have been issued for Cache Creek and the Sacramento-San Joaquin Delta Estuary recommending limited human consumption of sport fish because of elevated methyl mercury levels. Methyl mercury in fish is produced by sulfate reducing bacteria in sediment. The inorganic mercury concentration of sediment is an important factor controlling methyl mercury production by sulfate reducing bacteria. The Cache Creek watershed is about 2 percent of the landmass of the Central Valley but exports about sixty percent of the mercury. Half of the mercury from Cache Creek is trapped in the Cache Creek Settling Basin and the remainder is exported to the Delta. Therefore, understanding sources and distribution of mercury in Cache Creek and developing control programs to reduce exports is a high priority for the State of California.

The purpose of this study was threefold. First, conduct a survey of tributaries and flood plains in the Cache Creek canyon to ascertain the spatial distribution of mercury in their sediment. Second, use this information, if possible, to identify source(s). Finally, estimate the amount of mercury stored in the Canyon and available for downstream transport to the Cache Creek Settling Basin and the Delta.

The strategy for determining mercury sources was to identify tributaries with both elevated sediment mercury levels and higher concentrations downstream of their confluence with Cache Creek than above. One hundred and five sediment samples were collected and analyzed for mercury in the Cache Creek watershed between Clear Lake, Indian Valley Reservoir and the confluence of Bear Creek. There was no statistical difference in mercury concentration in sediment collected in the North Fork between Indian Valley Reservoir and the confluence with Cache Creek, between Clear Lake and the confluence with the North Fork and between the confluence of the North Fork of Cache Creek and Harley Gulch. The average background mercury concentration in sediment from the three areas was 0.06, 0.10, and 0.09-ppm in silt, sand and gravel sized material, respectively. Mercury concentration in Cache Creek increased statistically below Harley Gulch compared with upstream background concentrations. The average mercury concentration in 78 sediment samples collected in Cache Creek between Harley Gulch and Bear Creek was 0.98, 0.77 and 0.89-ppm in silt, sand, and gravel sized material, respectively. This represents an 8 to16-fold increase when compared with background levels above Harley Gulch. Sediment from the Harley Gulch delta, Crack Canyon and Davis Creek had statistically higher mercury concentrations than background material collected in Cache Creek above Harley Gulch. Mercury concentrations in silt and sand sized material from the Harley Gulch delta averaged 4.83 and 4.20-ppm, respectively. This is 81 and 42 times higher than background concentrations in similar sized material from above Harley Gulch. No gravel-sized material was collected in Harley Gulch.

The average mercury concentration in sand from Davis Creek was 0.84-ppm. Harley Gulch and Davis Creek are the only tributaries in the Cache Creek canyon with mercury mines. The source of contamination in Crack Canyon is not known but warrants investigation.

The mass of mercury in the Cache Creek canyon was calculated by multiplying the volume of sediment in depositional areas by its surface mercury concentration. Twenty-two hundred kg of mercury are calculated to be present in the 15-miles of canyon between Harley Gulch and Bear Creek. Eight hundred and fifty-five kg are estimated to be in depositional piles between Harley Gulch and Crack Canyon. The origin of this material is most likely from Abbott and Turkey Run mines in Harley Gulch as no other upstream source has been identified. The source of mercury in sediment below Davis Creek is likely a combination of inputs from mines in Harley Gulch and Davis Creek and from the unknown source in Crack canyon.

INTRODUCTION

Methyl mercury is a developmental toxin for humans and wildlife. The life stage most at risk is developing fetuses and young. The primary route of exposure is through consumption of methyl mercury-contaminated fish. A fish advisory has been issued for Cache Creek and the downstream Sacramento San Joaquin River Bay-Delta Estuary recommending limited human consumption of sport fish because of elevated mercury levels (California Office of Environmental Health Hazard Assessment, 2005; 2007). The advisories led the State of California to place Cache Creek and the Bay-Delta Estuary on the Federal Clean Water Act 303(d) list for impaired waters and prepare Total Maximum Daily Load (TMDL) reports to the U.S. EPA as required by federal statute (Wood *et al*., 2006; Cooke *et al*., 2004). A Basin Plan Amendment to control mercury has also been adopted by the Central Valley Regional Water Quality Control Board for Cache Creek as required by the State of California Porter-Cologne Water Quality Control Act (Cooke and Morris, 2005). The Basin Plan Amendment commits Regional Board staff to complete "*assessments…to determine whether responsible parties should be required to conduct feasibility studies to evaluate methods to control sources of mercury…Assessments are needed of stream beds and banks in…Cache Creek from Harley Gulch to Camp Haswell...".* This is the first of a series of assessment reports in fulfillment of the Basin Plan commitment.

The methyl mercury in fish is produced by sulfate reducing bacteria in sediment (Compeau and Bartha, 1985; Gilmour *et al*., 1992). All the factors controlling methyl mercury production by sulfate reducing bacteria are not known. However, the inorganic mercury content of the sediment is an important factor. The evidence is threefold. First, positive correlations exist between methyl and inorganic mercury concentrations in freshwater sediments, including the Bay-Delta Estuary (Heim, 2003). Inorganic mercury concentrations account for 19 percent of the variation in sediment methyl mercury concentrations in the Bay-Delta Estuary. More inorganic mercury results in more methyl mercury. While small, the positive correlation is statistically significant. The predictive ability of the relationship improves when comparisons are restricted to similar types of aquatic habitats and the total mercury concentration of the sediment is less than 1-ppm. Second, increasing concentrations of inorganic mercury have been added in the laboratory to sediment cores and increasing concentrations of methyl mercury measured in the overlying water (Bloom, 2003; Rudd *et al*., 1983; Kimball, 2005). These studies include mercury contaminated sediment from the Cache Creek drainage amended back into sediment from both Cache Creek and the Yolo Bypass (Bloom, 2003; Kimball, 2005). The experiments confirm that the inorganic mercury content of sediment is one factor controlling the rate of methyl mercury production by sulfate reducing bacteria. Finally, the methyl mercury concentration in fish at contaminated sites has declined after control measures were instituted to reduce incoming inorganic mercury loads (reviewed in Cooke *et al*., 2004). Together, the above three lines of evidence demonstrate that one method of reducing methyl mercury levels in fish is to reduce incoming loads of inorganic mercury and thereby reduce concentrations in sediment where bacteria reside.

The Cache Creek watershed is responsible for a disproportionate amount of all the mercury entering the Bay-Delta Estuary. A twenty-year mercury mass balance[1] has been calculated for the estuary (Wood *et al*., 2006). Cache Creek is about 2 percent of the landmass of the Central Valley but exports about sixty percent of the mercury. Half of the mercury from the Cache Creek watershed is trapped in the Cache Creek Settling Basin and the rest exported to the Yolo Bypass[2]. Mass balance calculations suggest that a significant part of the mercury transported by Cache Creek originates in the canyon between the confluence of the North Fork and Bear Creek (Foe and Croyle, 1998; Figure 1). However, the sum of tributary inputs in this critical reach only explains about twelve percent of the measured load (Cooke *et al*., 2004). The discrepancy is consistently greatest during winter high flow suggesting that the unknown source(s) may either be ephemeral streams that only flow in wet weather or that the loads predominately originate from erosion of contaminated bed and bank sediment not normally underwater and available for scour. Unfortunately, the 13-mile stretch of the Cache Creek canyon is very inaccessible making detailed wet weather studies impossible. Nonetheless, identification of wet weather sources is essential to determine whether they are controllable and might eventually constitute an option for reducing downstream mercury loads.

Inorganic mercury exported from Cache Creek contributes to methyl mercury production in wetlands in the Yolo Bypass. Wetlands are known to be efficient sites for the production of methyl mercury (as reviewed in Wiener *et al*., 2003). Several environmental organizations and the State of California have purchased land in the Yolo Bypass for wetland restorations. Recent purchases include the Vic Fazio Wildlife Refuge (16,000 acres), Liberty Island (10,000 acres) and Little Holland Tract (4,000 acres). Ongoing studies have confirmed that the Yolo Bypass is a major source of methyl mercury when flooded. Mass balance calculations indicate that the Bypass produced about 40 percent of all the methyl mercury discharged from the Sacramento watershed when flooded in the winter and spring of 2005/2006 (Foe *et al*., 2007). This is surprising as the Sacramento watershed is much larger than the Bypass[3]. Monitoring of small fish in the flooded Bypass demonstrated that they acquired some of the highest methyl mercury concentrations in the Central Valley and confirmed that the methyl

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[1] Mercury loads to the estuary are a function of water year (WY) type. More mercury is transported into the estuary in wet than dry years. WY 1984-2003 were selected for the mass balance calculation as the 20-year time period includes a mix of wet and dry years that are statistically similar to what has occurred in the Sacramento Basin since accurate water records began to be collected 100 years ago.

[2] Portions of the Yolo Bypass are within the legal boundary of the Sacramento-San Joaquin River Bay-Delta Estuary.

[3] The Yolo Bypass and Sacramento Basin are 59,000 and 16,765,000 acres, respectively. So, the Bypass is 0.4 percent of the landmass of the Sacramento Basin.

mercury was biologically available and being incorporated into the aquatic food chain (Slotton *et al*., 2007). The findings are disquieting and suggest that mercury contamination from upstream sources, such as Cache Creek, may complicate downstream wetland restoration. Therefore, controlling inorganic mercury loads that contribute to the disproportionate production of methyl mercury in the Bypass should become a high priority for the State of California.

The purpose of this study was threefold. First, survey tributaries and flood plains in the Cache Creek canyon to ascertain the spatial distribution of mercury in sediment. Second, use this information, if possible, to identify source(s). Finally, estimate the amount of mercury stored in the Canyon and available for downstream transport.

METHODS AND MATERIALS

Setting

Cache Creek is an eleven hundred square mile watershed in the California coast range (Figure 1). The basin is divided into three sub watersheds: the north and main forks of the Cache Creek and Bear Creek. All three water bodies flow year round. The north and main forks are regulated by dams at Indian Valley reservoir and Clear Lake, respectively. The reservoirs trap winter runoff for release in summer for agriculture. Bear Creek has no dams. Almost all the summer flow is diverted out of Cache Creek at Capay Dam. Controlled summer flows likely mobilize fine grain material from the creek bed and transport it to Capay dam where the material is diverted out of the channel and deposited on local farm land. During non-irrigation season (September to March) the inflatable dam at Capay is removed and larger more turbulent winter storm flows can scour contaminated sediment from the creek bed and transport it downstream to the Cache Creek Settling Basin and the Yolo Bypass.

The Cache Creek watershed includes portions of three historic mercury mining districts. Sulphur Bank Mine in the Clear Lake mercury mining district is the largest mercury mine in the watershed and is now a USEPA superfund site. Sulphur Bank Mine operated from 1875 to 1957 and is thought to have produced 4.7-million kg of mercury (Suchanek *et al*., 1997). About 0.1-million kg of mercury mine waste is now in sediment in Clear Lake (Suchanek *et al*., 1995) and may be available for transport down Cache Creek. The Sulfur Creek mining district consists of the Abbott-Turkey Run, Wide Awake, Manzanita, Empire, Central, Elgin, Clyde and Rathburn-Petray mercury mines. The Abbott-Turkey Run mine is in the Harley Gulch drainage while the Rathburn-Petray complex discharges to Bear Creek. The other mines drain to Sulfur Creek, which is tributary to Bear Creek. The Abbott-Turkey Run complex was the largest mining operation in the Sulfur Creek district and is estimated to have produced about 1.8-million kg of mercury (Churchill and Clinkenbeard, 2003). Production for the entire Sulfur Creek district is about 2-million kg. Finally, the Knoxville mercury mining district includes the Reed, Harrison and Manhattan mercury mines in the Davis Creek watershed. These mines operated from 1860 to 1978 and produced between 2.4 and 2.8-million kg of mercury (Lehrman, 1985). In 1984, the Homestake Mining Company purchased the site and impounded Davis Creek to create the Davis Creek reservoir to provide water for gold production. The Company also reclaimed mine waste and plugged the Reed mine adit. These action should have significantly reduced the off site movement of mercury. Nonetheless, annual monitoring of reservoir sediment demonstrates that Davis Creek Reservoir trapped an average of 72 kg of mercury per year for the 9 year period between 1993 and 2002 from the three upstream mines (Slotton *et al*., 2002). Off site movement of mercury prior to remediation and construction of the reservoir by Homestake may have been higher.

Mercury Inventory

During the winter of 2003 and again in 2004 Regional Board staff walked the Cache Creek canyon collecting sediment samples from major point bars and flood plains and from the mouth of tributary creeks to ascertain the distribution and mass of mercury in the canyon. Floodplains and creeks were identified *a priori* from an aerial photograph of the canyon provided by the California Department of Conservation (Appendix A). Three composite samples were collected in most instances from all large sediment deposits. Each composite was composed of 5 to 10 sub samples of about equal volume. Sub samples were collected with a trowel from the surface to a depth of about four inches over a 25-m^2 area. Care was taken to collect the composite samples from different elevations in each deposit to insure that the entire pile was characterized. Sediment samples from the tributaries were collected upstream of the high water mark from Cache Creek.

The weight of sediment in each deposit (kg) was estimated from equation 1:

(1) Weight (kg) = Elevation (m) x Surface Area (m^2) x 1530 (kg/m^3)

where elevation was the average height of the deposit above water level. Height was estimated during the field surveys. Surface area was computed from the aerial photograph using ArcView GIS software. A conversion factor of 1530 kg/m^3 was used to translate volumes of loosely mixed sand to weight (Dunn et al., 1981). The location, dimensions and weight of sediment in each depositional pile is provided in Tables B1 and B3 of Appendix B. Similar information for each tributary is in Table B2.

All composite samples were dried, homogenized and a known weight of material sequentially sieved through 65, 1,000, and 3,500-µm mesh screen. The size fractions were reweighed after sieving to estimate the fraction of the total weight each represented. A sub sample from each fraction was also submitted for mercury analysis. Size fractions less than 65, between 65 and 1,000 and between 1,000 and 3,500-µm are called silt, sand and gravel in this report[4].

The mercury content of each depositional pile was determined by summing the mercury content of the three size fractions (equation 2):

(2) $\sum \left(\text{Total Weight (kg) x Weight of Fraction}_i \text{ x Mercury Concentration of fraction}_i \text{ (mg/kg)}\right)$
i=3 size fractions

Where Total Weight is the estimated weight of the flood plain deposit from equation (1). The Weight of Fraction_i and Mercury concentration of Fraction_i are the proportion of the total weight and the mercury concentration of each size fraction, respectively. The mass of mercury in each deposit was estimated by summing the mercury mass of each fraction and averaging the values for the three composites. The inventory of mercury in each depositional pile in the Cache Creek Canyon is summarized in Table B3.

Knowledge about the mercury content of each size fraction may be helpful in understanding the fate of the material (Knighten, 1992). Fine grained material, like silt, is readily transported by laminar flow such as occurs in Cache Creek in summer. In contrast, larger sand and gravel type material can only be moved up into the water column by more turbulent flow and usually must be broken down into smaller particles by physical and chemical weathering before being transported downstream.

Mercury Analysis

The mercury concentrations of sediment samples were analyzed by two laboratories. ALS Chemex[5], a certified analytical company specializing in assaying mine grade material, analyzed the samples collected in 2003 using cold vapor atomic absorption (EPA method 245.5). Because of possible quality assurance/quality control problems, all subsequent analysis was performed by the California Department of Fish and Game at Moss Landing Marine Laboratories[6]. Moss Landing Marine Laboratories analyzed mercury using a flow injection mercury system (CALFED, 2000). Standard reference material and duplicate field samples were analyzed by each laboratory to estimate accuracy and precision. All results are reported as mg mercury per kg dry weight sediment or (ppm).

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[4] Technically, silt are all particles less than 64-µ, sand between 64 and 2,000 µm and gravel greater than 2,000µm (Knighton, 1984)

[5] ALS Chemex, 994 Glendale Ave, Unit 3, Sparks, Nevada 89431-5730

[6] Moss Landing Marine Laboratories, 7544 Sandholdt Road, Moss Landing, CA 95039

Statistics

Differences in sediment mercury concentration were analyzed with non-parametric statistics as transformations could not be found to eliminate the strong correlations between means and variances. Statistica software was employed for all the statistical analysis[7] .

RESULTS AND DISCUSSION

Quality Assurance/Quality Control Program

The program assessed the accuracy and precision of laboratory measurements. Accuracy was measured by both the analysis of standard reference material with a certified mercury content and by amending a known amount of mercury into Cache Creek sediment and measuring the percent recovery. Precision was measured by repeated analyses of laboratory and field duplicates. The accuracy and precision of ALS and MLML were satisfactory and the results adequate for estimating mercury concentrations and loads in the Cache Creek canyon. Results from the quality assurance/quality control program are summarized more fully in Appendix C.

Source and Distribution of Mercury

The primary source(s) of mercury in Cache Creek were identified by measuring concentrations in sediment deposits in the Creek canyon and in all tributaries. The strategy for determining mercury sources was to identify tributaries with both elevated sediment mercury levels and an increase in sediment concentration downstream of the confluence with Cache Creek than above.

Background mercury concentration in sediment in Cache Creek above the confluence of Harley Gulch was ascertained from sediment samples collected from the North Fork of Cache Creek between Indian Valley Reservoir and the confluence with Cache Creek, from Cache Creek above the confluence with the North Fork, and from Cache Creek between the North Fork and Harley Gulch (Figure 1b and Table 1). There was no difference in mercury concentration in sediment collected between the confluence of the North Fork and Harley Gulch and from either of the other two upstream reaches of the Creek ($P>0.05$, Kruskal-Wallis test). The average background concentration in 14 samples collected from the watershed above the confluence of Harley Gulch was 0.06, 0.10, and 0.09-ppm mercury in silt, sand, and gravel sized material, respectively.

Clear Lake is one of the most mercury contaminated freshwater lakes in the world (Suchanek *et al*., 1997). Sediment mercury concentrations in the Oaks Arm near Sulphur Bank mine are as high as 400-ppm. Concentrations decrease

[7] Statistica StatSoft, http:// www.statsoft.com

to 1 to 10-ppm mercury in the Lower Arm where water is discharged through the dam to Cache Creek. The finding in this study that sediment mercury levels in Cache Creek below the Clear Lake dam are low is consistent with earlier observations that only small mercury loads leave the dam (Foe and Croyle, 1998). Apparently, most of the mercury from Sulphur Bank mine is being sequestered in Clear Lake and is not discharged to Cache Creek. The mercury leaving Clear Lake is likely carried on silt-sized material and is efficiently transported through the Cache Creek canyon.

Mercury concentration increases in sediment in Cache Creek below Harley Gulch when compared with background levels from the upper watershed (Table 1). The increase is statistically significant for silt collected in Cache Creek between Jack and Judge Davis Creeks, Trout and Crack Creeks, Crack and Davis Creeks, and Davis and Bear Creeks ($P<0.01$, Kruskal-Wallis Test). For sand the increase is significant between Trout and Crack Creeks and Davis and Bear Creeks ($P<0.001$, Kruskal-Wallis Test). Finally, for gravel the increase is significant for reaches of the Creek between Trout and Crack Creeks, Crack and Davis Creeks, and Davis and Bear Creeks ($P<0.05$, Kruskal-Wallis Test). Average mercury concentration in 78 sediment samples collected from Cache Creek between Harley Gulch and Bear Creek is 0.98, 0.77 and 0.89-ppm in silt, sand and gravel sized material, respectively. These values represent a 16, 8, and 10-fold increase for each of the three size fractions compared with background levels for the watershed above Harley Gulch.

Sediment samples were collected from each tributary in the Cache Creek Canyon and analyzed for mercury. Harley Gulch, Crack Canyon and Davis Creek had higher concentrations than the background level measured in the watershed above Harley Gulch (Table 2). Mercury concentrations in silt and sand sized material from the Harley Gulch delta averaged 4.83 and 4.20-ppm, respectively (Ichikawa and Jakl, 2004). No gravel-sized material was collected for analysis from Harley Gulch. Mercury concentrations in silt and sand from Harley Gulch are 81 and 42 times higher than background levels in similar sized material from the upper watershed. Both differences are statistically significant ($P<0.0001$, Kruskal-Wallis test). Mercury concentrations in gravel from Crack Canyon were elevated when compared to background levels from the upper basin ($P<0.05$, Kruskal-Wallis test). The gravel sized material averaged 0.38-ppm mercury. This represents a 4-fold increase above background levels measured in upper Cache Creek. Finally, mercury concentration in sand sized material from Davis Creek is also elevated when compared to concentrations from the upper watershed. The average mercury concentration in sand from Davis Creek is 0.84-ppm. The difference is significant when compared to background levels in sand in the upper Cache Creek watershed ($P<0.05$, Kruskal-Wallis test). Harley Gulch and Davis Creek are the only tributaries to this section of the Cache Creek canyon with mercury mines. The source of the contamination in Crack Canyon is not known but warrants investigation.

Mercury mines in Harley Gulch and Davis Creek are known to have erosive sediment with elevated mercury levels. Mercury concentrations in mine waste at Abbott and Turkey Run have been measured in the hundreds of ppm (Churchill and Clinkenbeard, 2003). An investigation was undertaken to determine whether there might be other tributary sources of mercury in the Harley Gulch drainage and none was found (Ichikawa and Jakl, 2004). So, the high concentration of mercury in sediment in the depositional zone at the confluence of Harley Gulch and Cache Creek must have originated from the two upstream mines. The elevated mercury levels in Cache Creek sediment for seven miles between Harley Gulch and Crack Canyon must also have come from the Abbott and Turkey Run mines as no other upstream source has been identified.

Slotton *et al*. (2002) have measured sediment mercury concentrations annually for nine years in Davis Creek reservoir. The reservoir is located below the Reed, Harrison and Manhattan mercury mines. Sediment concentrations range between 0.1 and 94.7-ppm with a 9-year whole reservoir average of 2.1-ppm mercury. Many of these values were obtained after Homestake removed contaminated waste piles from the abandoned mine sites and sealed the adit from the Reed mine. Presumably, sediment with similar or higher mercury concentrations may have been exported from the Davis Creek watershed prior to construction of the dam. So, elevated mercury in sediment in Cache Creek downstream of Davis Creek is most parsimoniously explained as a mix of inputs from Abbott and Turkey Run mines, Crack Canyon and the Reed, Manhattan and Harrison mines.

Mercury Inventory

Four holes were dug in depositional sediment piles and samples taken at increasing depth to determine whether mercury concentration changed as a function of depth. The location of the holes were in the Harley Gulch delta, between Rocky and Harley Gulch, between Crack and Davis Creek, and downstream of Davis Creek (Figure 1). The data for the Harley Gulch delta is from Ichikawa and Jakl (2004). Replicate samples for mercury analysis were only taken in holes dug in the Harley Gulch delta and downstream of Davis Creek. So, a within-hole statistical analysis is only possible at these two locations. No change in mercury concentration was detected in any size fraction as a function of depth at either location ($P>0.08$, Kruskal-Wallis test; Figure 2). Next, data from all four holes were combined and a regression analysis performed to assess whether there was evidence that concentrations changed in all the holes with depth (Figure 3). The mercury content of silt and sand decreased with increasing depth while gravel concentrations increased. However, none of the slopes were statistically different from zero, again, suggesting that mercury concentration is independent of depth. Therefore, the assumption is made here that the entire mass of all depositional piles has the same mercury concentration as was measured in their surface sediment.

The mass of mercury in the canyon was calculated by multiplying the volume of sediment in depositional areas by its surface mercury concentration. The largest volumes of sediment were found in flatter areas of the canyon with broader floodplains. In particular, Wilson Valley between Rocky and Judge Davis Creeks, Kennedy Flat between Trout and Crack Canyon, and the area below Davis Creek have large deposits of sediment (Appendix A, Table 3). These areas also contained the largest amounts of mercury. However, on a-per-weight basis, the mercury content of sediment is greatest below the confluence of Davis Creek (Table 1). Higher mercury concentrations below Davis Creek may be because sediment from Davis Creek was historically more contaminated than what arrived from upstream and some of the Davis Creek material is still there or because much of the sediment from the upper basin, including Harley Gulch, has not yet had time to travel beyond this point.

The study estimates that about 2,200 kg of mercury are present in the 15-miles of canyon between Harley Gulch and Bear Creek (Table 3). This estimate does not include the 15 to 20-kg of mercury contained in the Harley Gulch delta (Cooke and Morris, 2005). Eight hundred and fifty-five kg are estimated to be in depositional piles between Harley Gulch and Crack Canyon. The origin of this material is most likely from Abbott and Turkey Run mines in Harley Gulch. The source of the mercury below Davis Creek is likely a combination of inputs from Abbott and Turkey Run, Reed, Manhattan and Harrison mercury mines and the unknown source in Crack canyon.

Uncertainty about the 2,200-kg mercury inventory for the Canyon may range between a low of about half this value to, perhaps, twice the amount. The lower value (1,100-kg) is estimated from observations that, perhaps, up to half the sediment in depositional areas is cobble and larger sized material and has little or no associated mercury. The upper value (4,400-kg) results from the fact that almost none of the smaller depositional piles have been sampled. These likely have a mercury-content similar to adjoining larger deposits that were assayed, but their combined mass has not been estimated and their mercury content included in the 2,200-kg estimate. Our best professional judgment is, after walking the canyon twice, that the combined volume of all the smaller unmeasured deposits is not likely to exceed the volume of material already sampled.

The mercury inventory in the Cache Creek canyon can be compared with the amount of mercury produced and lost in the watershed during mining. Historically, mercury mining was inefficient and up to 25 percent of the processed material may have been lost to the environment (Churchill, 1999). Major losses occurred in retort furnaces and calcine waste piles. Not all the lost material was transported to local creeks. Sulphur Bank mine in Clear Lake may be considered as an example. The mine is estimated to have produced about 4.7 million kg of mercury and about 0.1 million kg is now sequestered in lake sediment (Suchanek *et al*., 1995, 1997). If it is assumed that all the mercury lost to water now resides in Clear Lake, then about 2 percent of the total production was lost to the aquatic environment[8]. Mercury production in Harley Gulch and Davis Creek are estimated to between 4.2 to 4.6 million kg (Lehrman, 1985; Churchill and Clinkenbeard, 2003). If 1 to 2 percent of their production was lost to the aquatic environment, then losses to Cache Creek would be between 42,000 and 84,000 kg of mercury. The inventory of mercury in the Cache Creek canyon is 2,200 kg or 3-6 percent of this amount. Churchill and Clinkenbeard (2003) estimate that 51,000 to 53,000 kg of mercury remain in calcine piles in the Sulfur Creek mining district. The U.S. EPA CERCLA action is reported to have stabilized 400,000 cubic yards of mine waste at the Abbott Turkey Run mine complex in the Sulfur Creek mining district (USEPA Region 9, 2007). This may have prevented eventual off site movement of between 68,000 and 110,000 kg of mercury[9]. No estimate is available for the amount of mine waste at the Davis Creek mining complex. By comparison, the TMDL for the Bay-Delta estuary estimates that 240 kg per year are exported from the Cache Creek watershed (Wood *et al.,* 2006). Obviously, all these calculations are rough but they place the Cache Creek canyon mercury inventory in perspective.

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[8] (100,000 kg lost/4,700,000 kg produced) x 100

[9] Average mercury content of Abbott and Turkey Run waste rock and mining tailing piles are between 143 and 238 ppm mercury (27 June 2006 letter from Iain Baker to Janet Yocum). This translates to between 68,000 and 110,000 kg of mercury in the 400,000 cubic yards of stabilized mine waste.

Grain size analysis reveals that more than 75 percent of the mercury in the Cache Creek canyon is contained in sand and larger sized material (Table 3). This material is only mobilized and transported in the wash load during higher, more turbulent flow (Knighton, 1992). The finding that most of the mercury is contained in larger size fractions is consistent with earlier observations that large loads of mercury only originate from the canyon during high runoff events (Foe and Croyle, 1998) and suggests that erosion of larger sized depositional material may be part of the explanation for larger loads during high flow. A second possible explanation is that some of the mercury observed at the exit to the Cache Creek canyon may originate in the eight miles between the Davis Creek reservoir Dam and the confluence with Cache Creek. No study has yet attempted to measure mercury loads exiting from Davis Creek at its confluence with Cache Creek during high flow. It is possible that high flows in Davis Creek are also scouring historic mine waste and transporting it downstream. The Regional Board should make it a high priority to inventory mercury loads in the Davis Creek watershed and conduct a loading study to determine whether significant amounts of mercury are being scoured from the watershed and transported to Cache Creek during storm events.

Cache Creek continues for 48-miles after the confluence with Bear Creek before discharging into the Cache Creek Settling Basin and the Yolo Bypass. Average sediment mercury concentrations in the Settling Basin range between 0.32 and 0.34-ppm (Table B1). This is 4 to 5 times less than the concentration below Davis Creek (Table 1). The decrease is attributed to influx of sediment with low mercury concentrations in creeks and sloughs on the Capay Valley floor (Foe and Croyle, 1998). These dilute sediment with higher mercury levels from the Cache Creek Canyon. Nonetheless, the concentrations in the Settling Basin are 3 to 5 times higher than occur in background material above the confluence of Harley Gulch. No attempt has yet been made to inventory the mercury content of depositional areas in Cache Creek downstream of the confluence of Bear Creek. However, such a sampling effort would likely increase by many-fold the amount of mine waste that has moved off site from the mining districts and now contaminates the Cache Creek drainage.

The Basin Plan amendment for Cache Creek requires Board staff to do assessments to determine whether land owners and other responsible parties should be required to conduct feasibility studies to evaluate methods to control and remediate mercury sources in the watershed (Central Valley Regional Water Quality Control Board, 2007). The Executive Officer of the Regional Board will prioritize the need for feasibility studies and subsequent remediation actions based on mercury concentrations and masses, erosion potential, and accessibility. Following review of the feasibility studies, the Executive Officer will determine whether cleanup actions will be required.

The Executive Officer will, based on this report and any additional information, evaluate whether to require responsible parties to prepare feasibility studies to evaluate the potential to trap and/or remove mercury contaminated sediment from the Harley Gulch delta and from the Cache Creek canyon below the confluence with Davis Creek. These areas have the highest mercury masses and concentrations in the watershed. In addition, there may be access to the Cache Creek canyon below Davis Creek through the Langs Peak Road to Buck Island. It is recommended that Regional Board staff conduct assessments of Crack Canyon, Davis Creek between the reservoir and Cache Creek, and Cache Creek below the confluence of Bear Creek. The goal of these studies should be to identify areas with large mercury deposits that can be economically remediated to reduce the loads of mercury now being exported from the Cache Creek drainage. Reduction of mercury loads from Cache Creek is expected to reduce methyl mercury production in the Yolo Bypass and downstream in the Bay-Delta Estuary.

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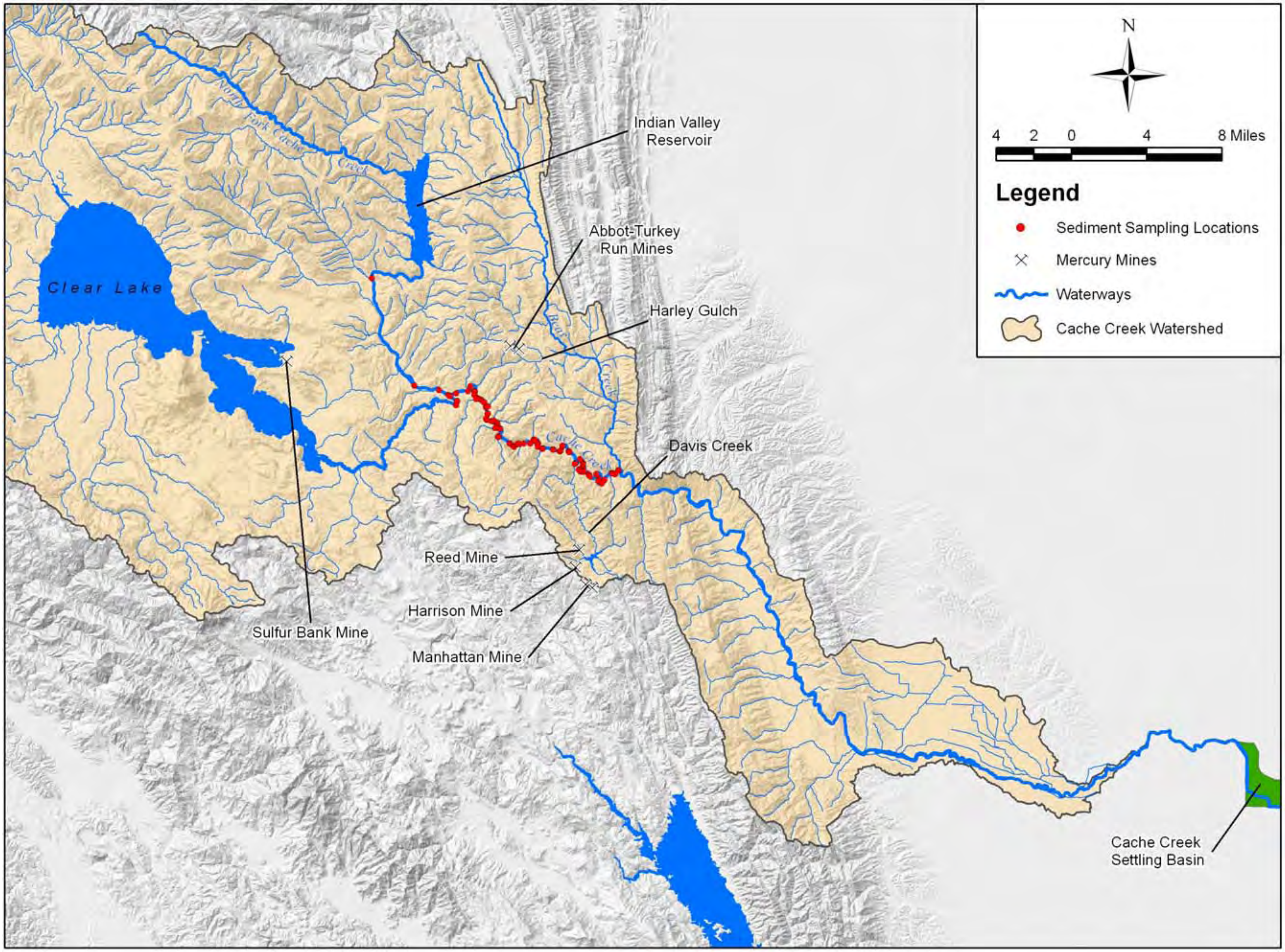


Figure1a: Overview of the Cache Creek Watershed and Sediment Sampling Locations

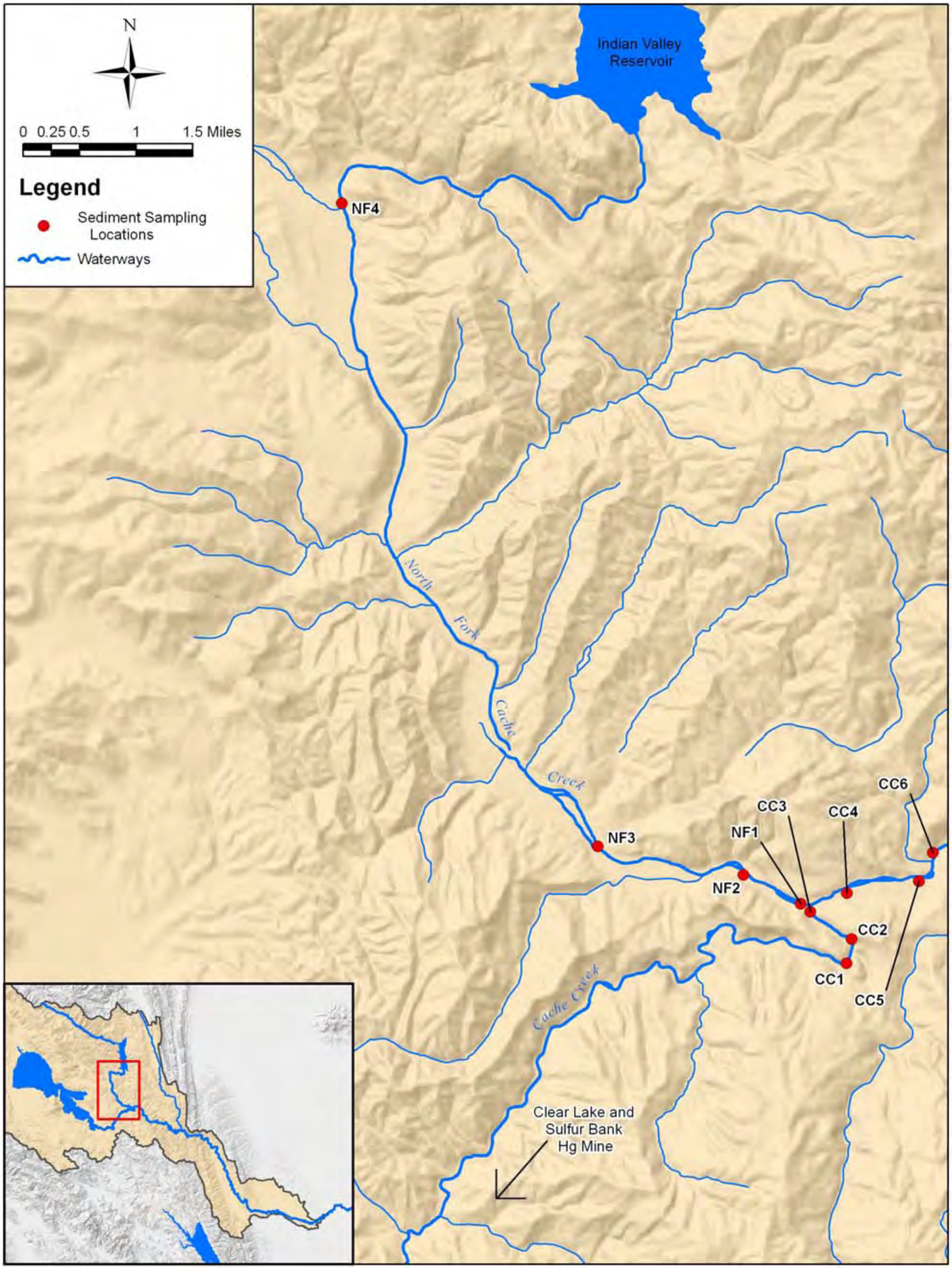


Figure 1b: Sediment Sampling Locations from Cache Creek, North Fork downstream to Bear Creek

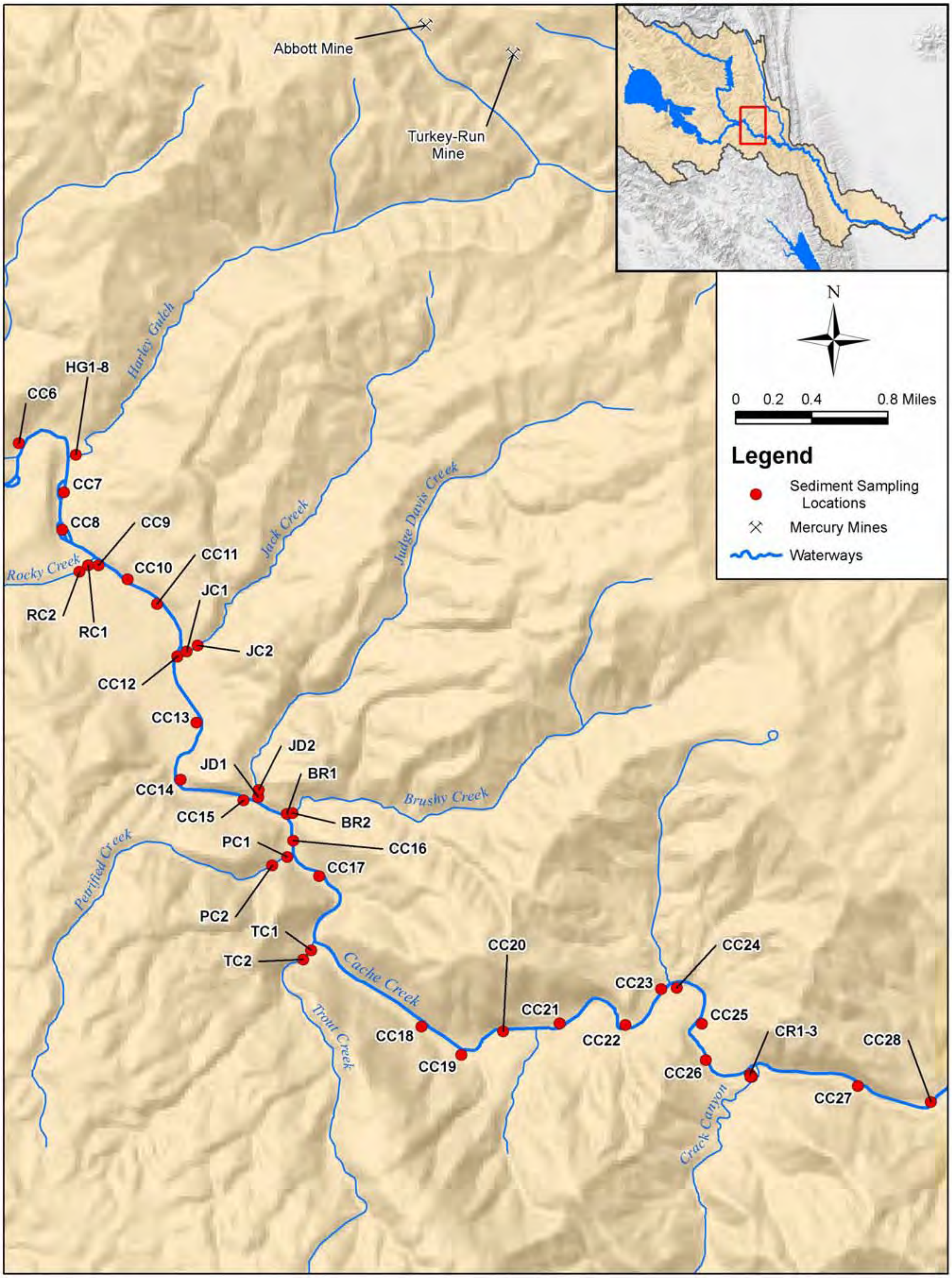


Figure 1c (Continued)

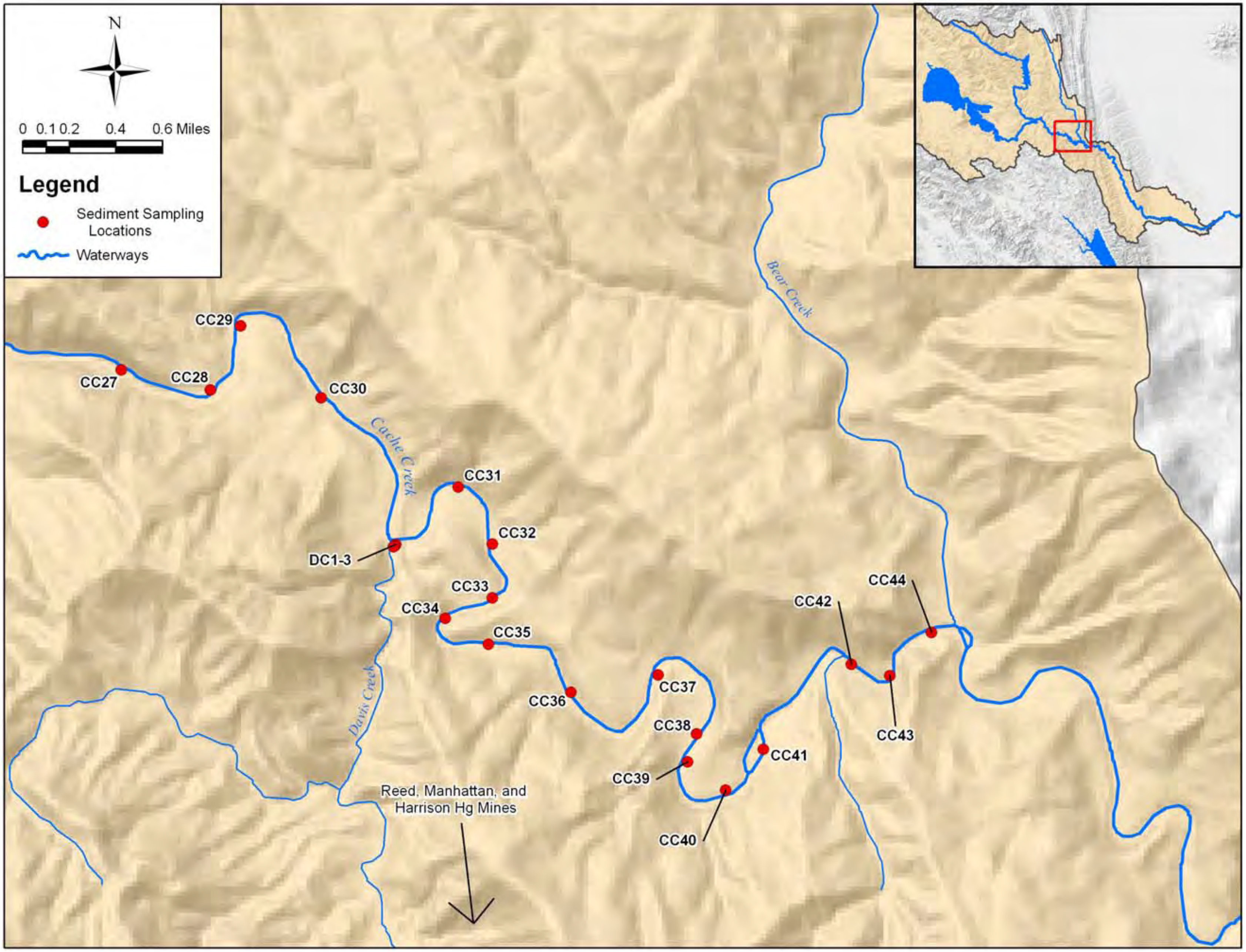
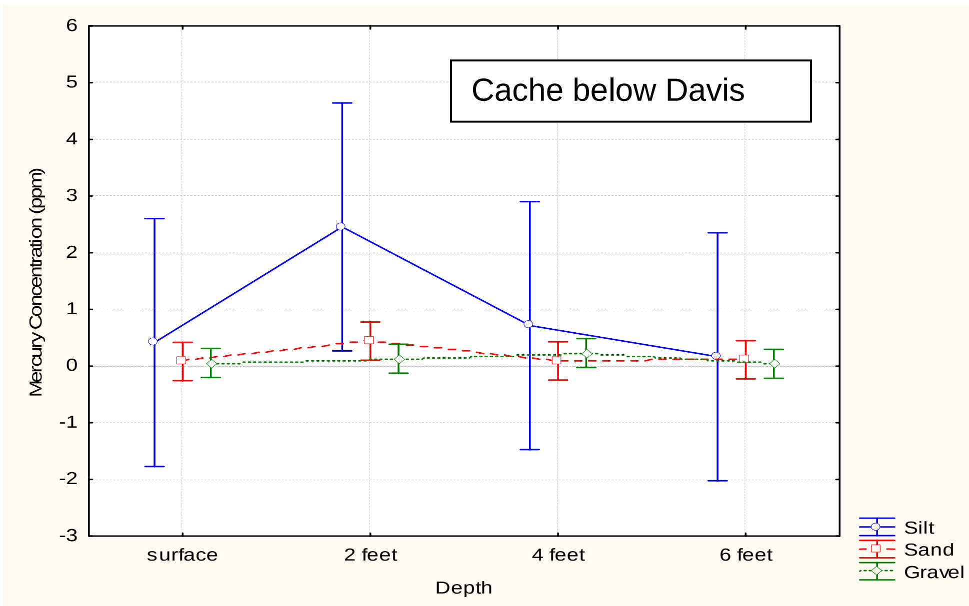


Figure 1d (Continued)

Figure 2 Mercury concentration (ppm) as a function of depth in holes dug in a depositional pile in Cache Creek below the confluence of Davis Creek and in the Harley Gulch delta. Vertical bars are 95 percent confidence intervals



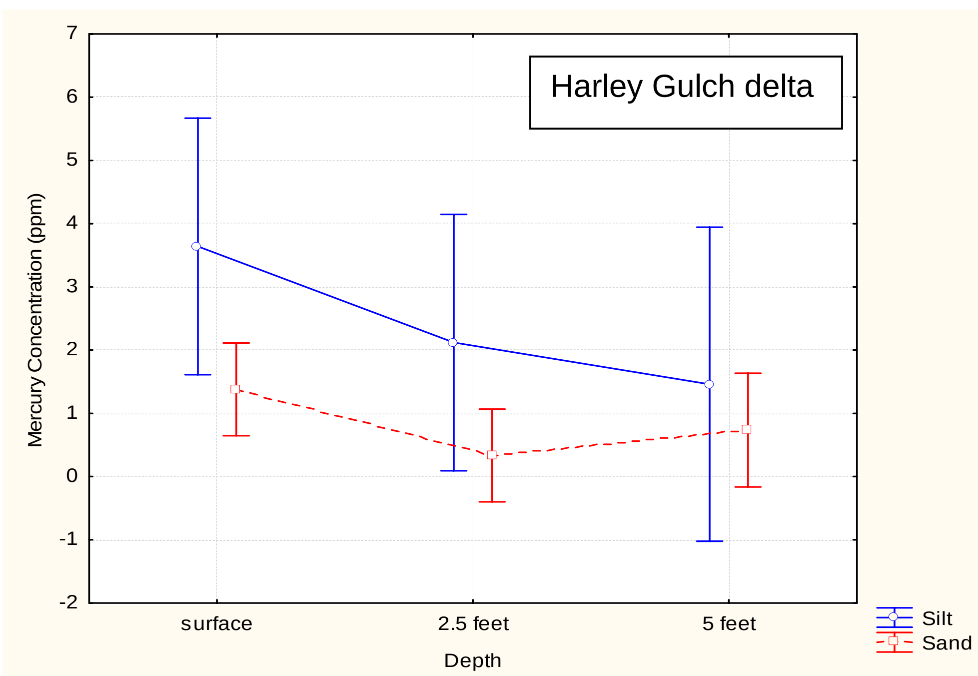


Figure 3   Mercury concentration in holes dug in the Cache Creek Canyon

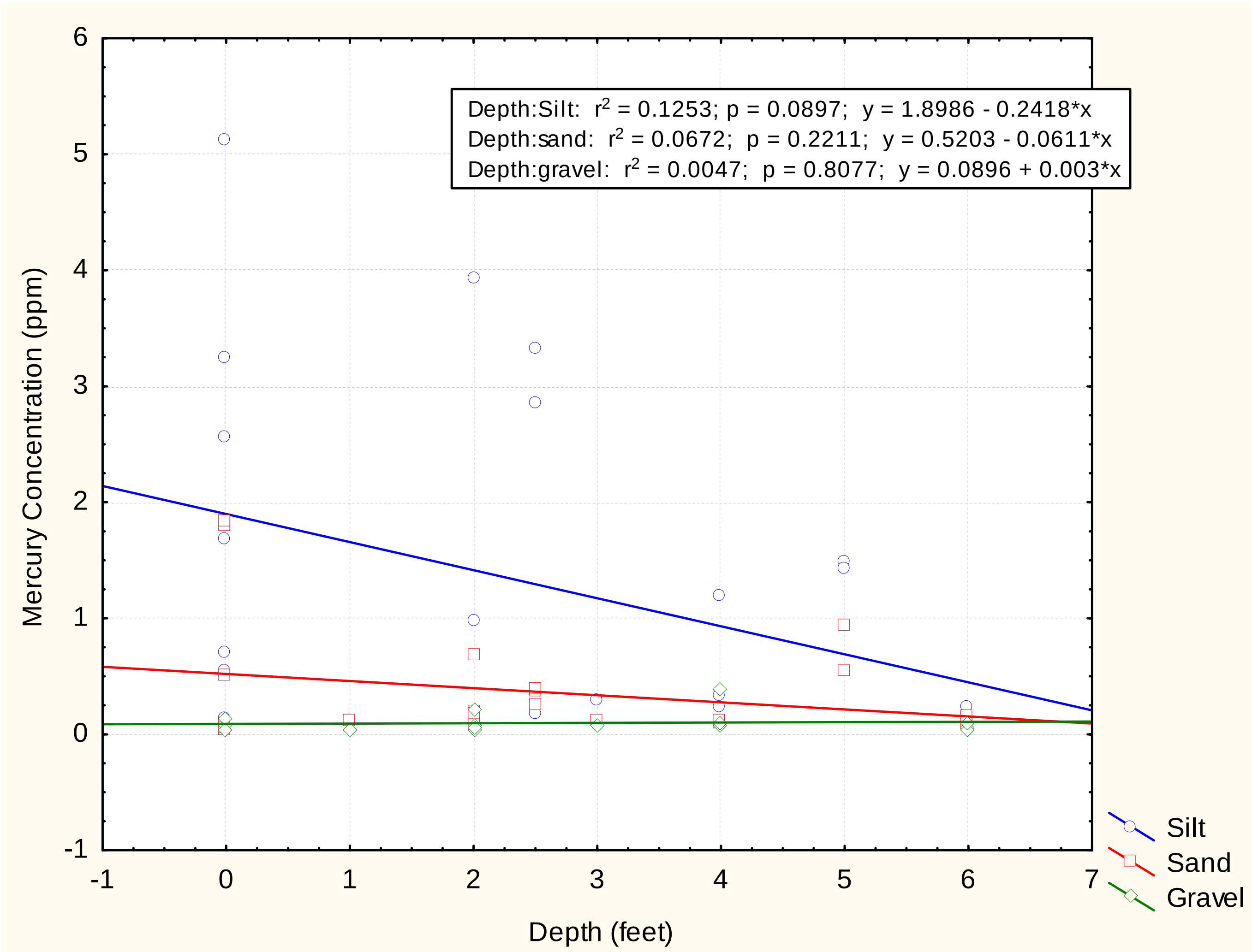


Table 1. Mercury concentration (ppm) in sediment collected from the main stem of Cache Creek (see Figure 1 for site locations and Table B1 for raw data). Creek reaches with an asterisk have statistically higher concentrations than occur in similar grain size material in Cache Creek above the confluence of Harley Gulch (see text for details). Average background mercury concentrations in silt, sand, and gravel above Harley Gulch are 0.06, 0.10, and 0.09-ppm mercury, respectively.

		Average Hg Concentration (ppm)[1/]		
Reach	# Samples	Silt	Sand	Gravel
North Fork	4	0.04	0.06	0.09
Cache above North Fork confluence	7	0.08	0.07	0.10
Cache between confluence & Harley	3	0.05	0.22	0.05
Cache between Harley Gulch & Rocky	4	0.44	0.06	0.36
Cache between Rocky & Jack	8	0.51	0.43	0.09
Cache between Jack & Judge Davis	10	0.64**	0.39	0.28
Cache between Judge Davis & Petrified	3	0.88	0.08	0.05
Cache between Petrified & Trout	3	0.09	0.08	0.09
Cache between Trout & Crack	15	1.02***	0.85***	0.99***
Cache between Crack & Davis	10	0.89***	0.47	0.38*
Cache between Davis and Bear	25	1.51***	1.35***	1.66*

[1/] * P<0.05, **P<0.01, ***P<0.001

Table 2. Mercury concentration (ppm) in sediment collected from all large tributaries to Cache Creek between the confluence of the North Fork and Bear Creek. Tributaries with an asterisk have statistically higher concentrations than occur in similar size material from the watershed above the confluence of Harley Gulch (see text for details). Average background mercury concentrations in silt, sand, and gravel in Cache Creek above Harley Gulch are 0.06, 0.10, and 0.09-ppm mercury, respectively. Mercury concentrations for Stemple Creek and the Harley Gulch delta are from Ichikawa and Jakl (2004).

		Average Hg Concentration (ppm)[1/]		
Tributary	# samples	Silt	Sand	Gravel
Stemple Creek	2	0.06		
Harley Gulch delta	8	4.83***	4.21***	
Rocky Creek	2	0.10	0.10	0.33
Jack Creek	2	0.06	0.06	0.05
Judge Davis Creek	3	0.36	0.18	0.28
Bushy Creek	2	0.04	0.25	0.14
Petrified Creek	2	0.09	0.07	0.09
Trout Creek	2	0.15	0.14	0.12
Crack Canyon	4	0.19	0.40	0.38*
Davis Creek	4	0.72	0.84*	0.34

[1/] * $P<0.05$, *** $P<0.0001$

Table 3. Inventory of mercury (kg) in sediment deposits in the Cache Creek Canyon

		Mercury Mass (kg)			
Reach	Sediment volume (m^3)	Silt	Sand	Gravel	Total
Cache between Harley & Rocky	76,122	4	6	2	12
Cache between Rocky & Jack	147,315	9	49	1	59
Cache between Jack & Judge Davis	224,941	15	127	2	144
Cache between Judge Davis & Petrified	16,634	1	2	0	3
Cache between Petrified & Trout	12,927	0	1	0	1
Cache between Trout & Crack	443,664	111	397	61	569
Cache between Crack & Davis	127,705	20	39	8	67
Cache between Davis and Bear	541,589	182	1,069	88	1,339
Total	**1,600,000**	**340**	**1,700**	**160**	**2,200**

APPENDIX A

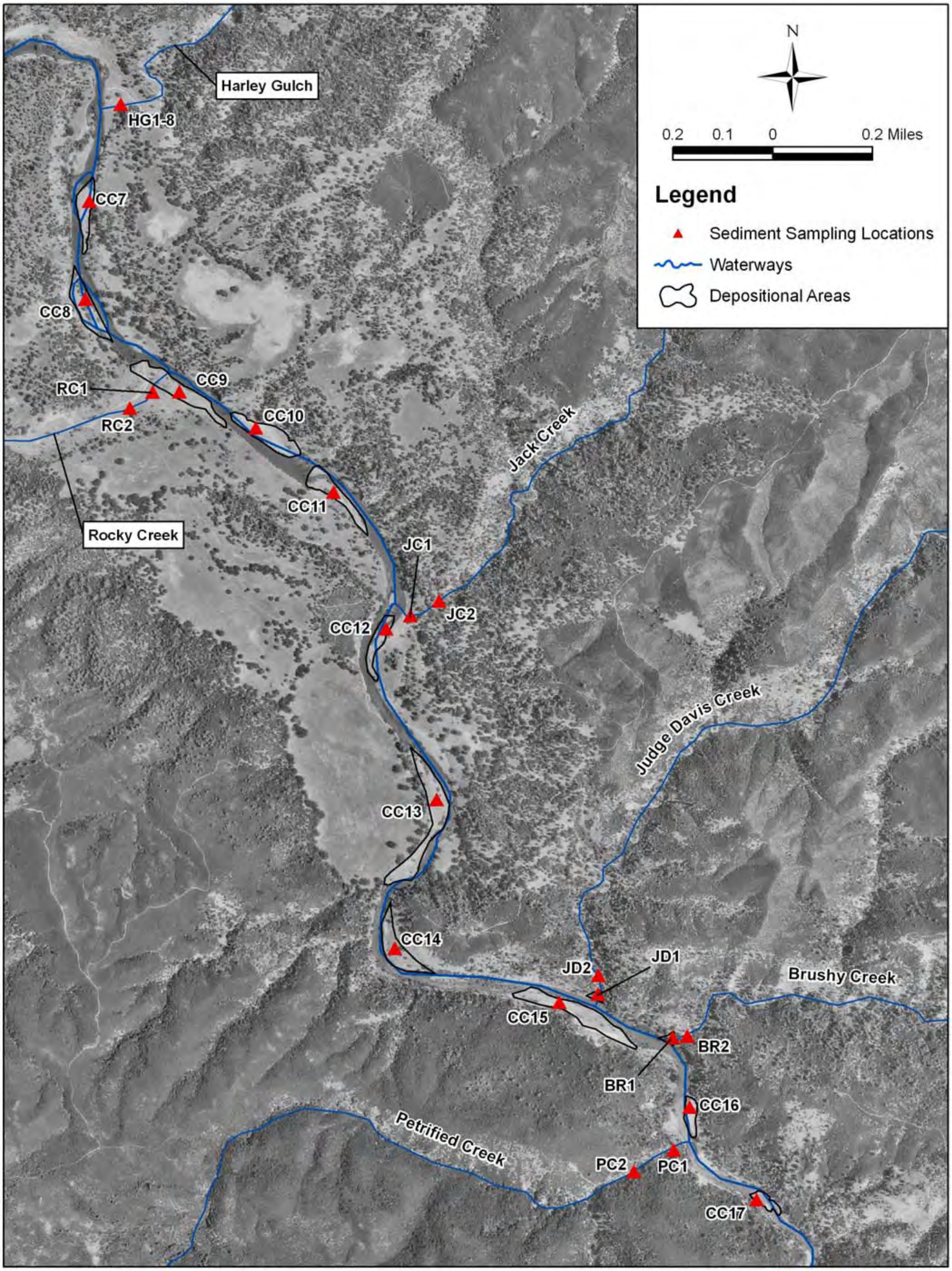


Figure 1a: Map of Cache Creek Canyon showing sampling sites from Harley Gulch down to Bear Creek

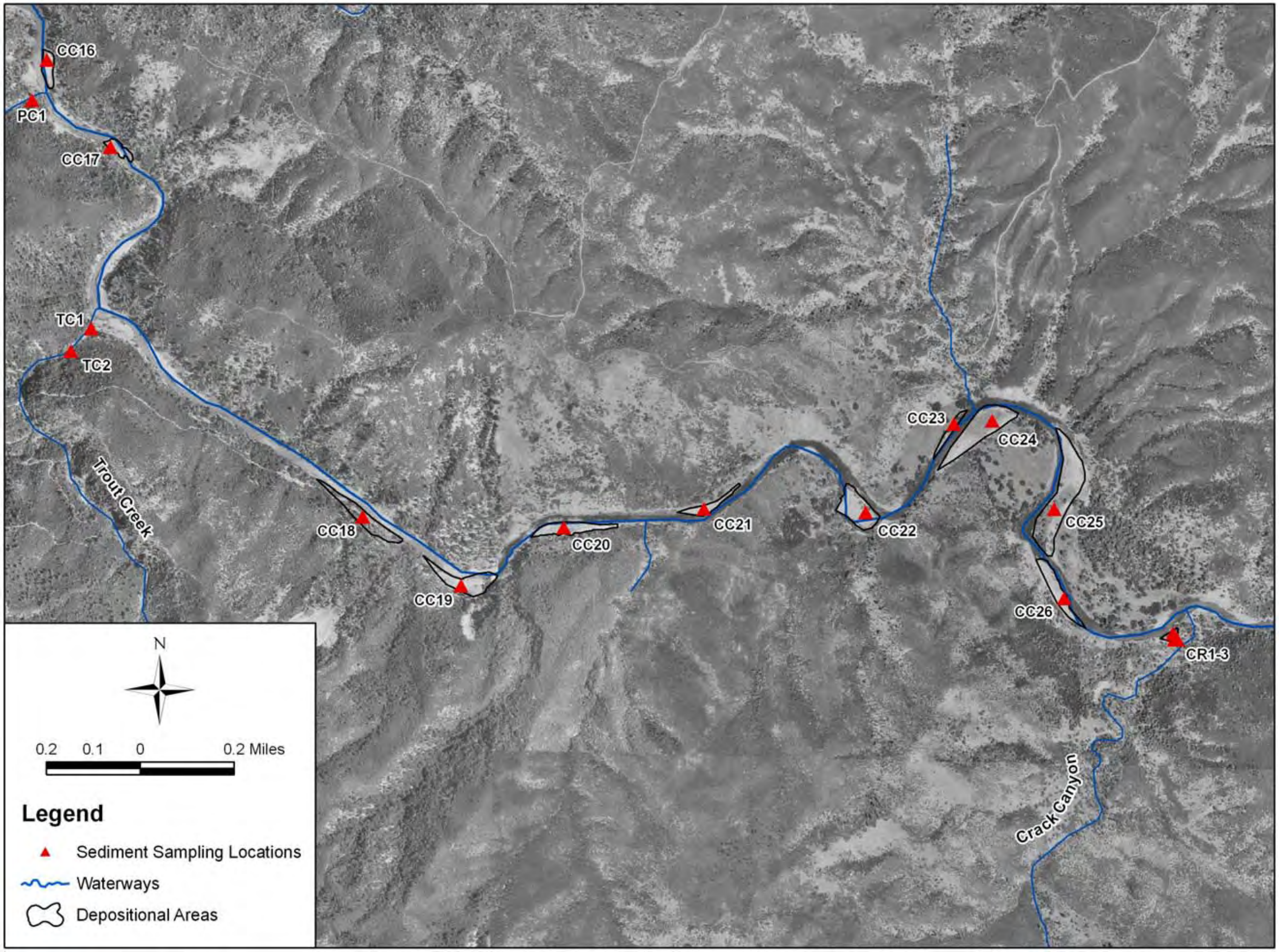


Figure 1b (Continued)

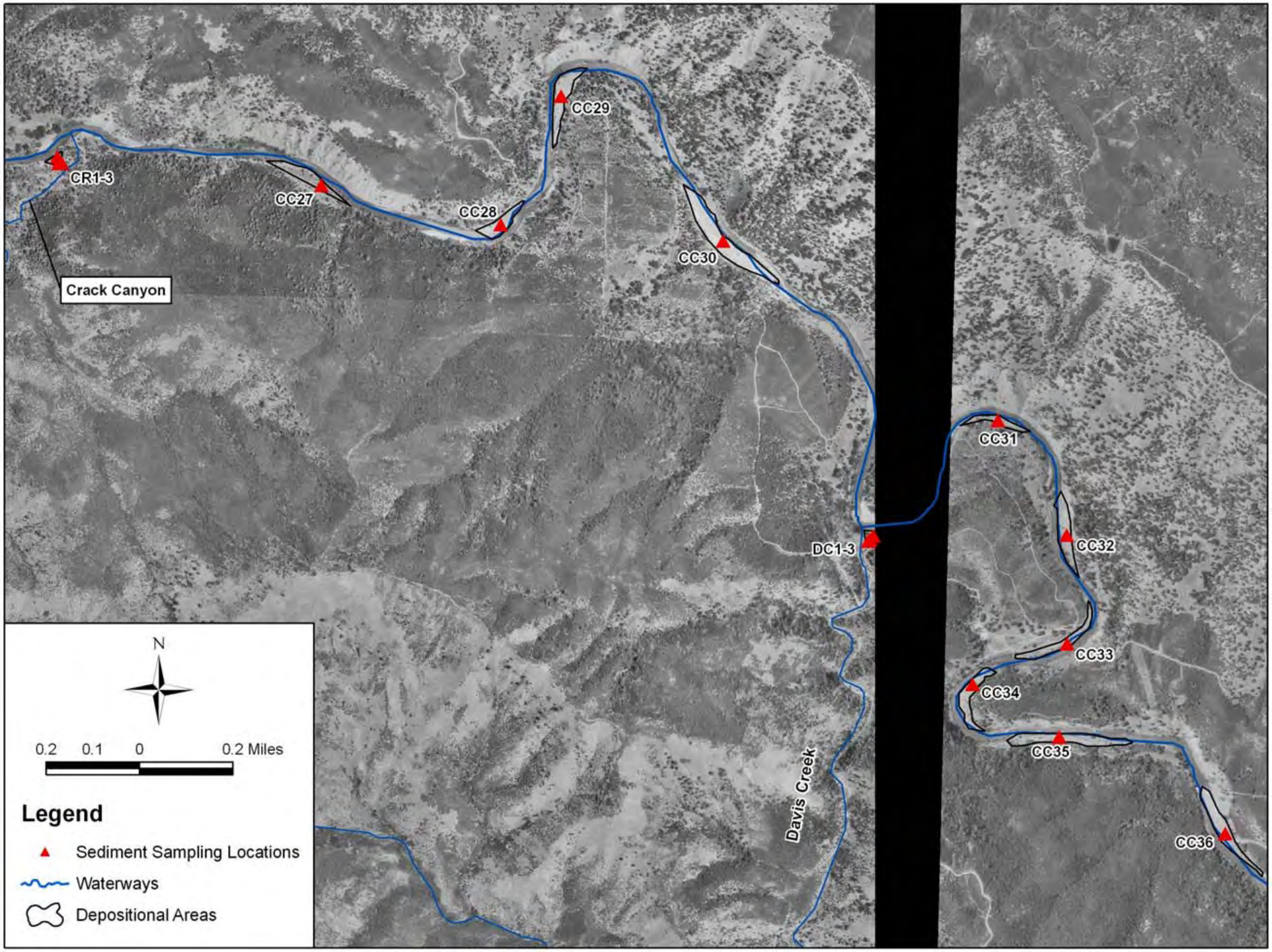


Figure 1c (Continued)

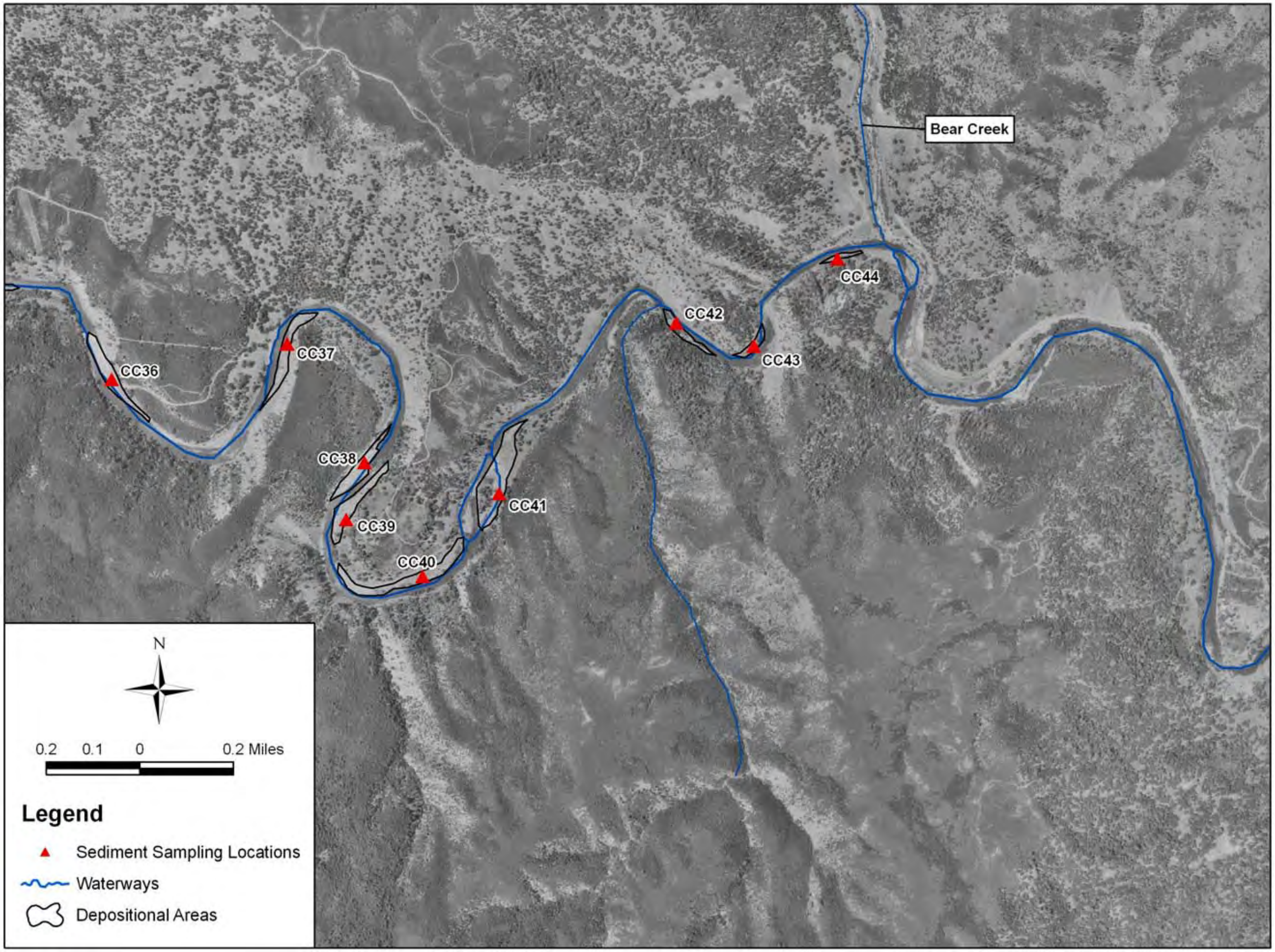


Figure 1d (Continued)

APPENDIX B

Table B1. Summary of mercury concentrations by grain size in Cache Creek.

Station Code	Replicate	Creek Reach	Latitude	Longitude	Percent of total sample weight			Mercury concentration (ppm)			Mercury Analytical Lab
					Silt	Sand	Gravel	Silt	Sand	Gravel	
CC1	A	Cache above N Fk	38.97346	122.49733	17%	77%		0.06	0.04		MLML
CC2	A	Cache above N Fk	38.97658	122.49657	10%	65%	25%	0.08	0.06	0.07	MLML
CC2	B	Cache above N Fk	38.97658	122.49657	28%	72%		0.09	0.09		MLML
CC2	C	Cache above N Fk	38.97658	122.49657	7%	51%	42%	0.07	0.08	0.08	MLML
CC3	A	Cache above N Fk	38.97996	122.50350	15%	73%	12%	0.1	0.08	0.21	MLML
CC3	B	Cache above N Fk	38.97996	122.50350	12%	61%	27%	0.08	0.08	0.08	MLML
CC3	C	Cache above N Fk	38.97996	122.50350	11%	52%	37%	0.09	0.08	0.08	MLML
NF1	A	North Fork-Cache	38.98097	122.50511	39%	43%	3%	0.03	0.03	0.03	MLML
NF2	A	North Fork-Cache	38.98447	122.51469	23%	66%	5%	0.03	0.02	0.13	MLML
NF3	A	North Fork-Cache	38.98767	122.53883	22%	58%	8%	0.03	0.07	0.09	MLML
NF4	A	North Fork-Cache	39.06953	122.58406	41%	29%	8%	0.08	0.13	0.13	MLML
CC4	A	N fork-Stemple	38.98372	122.49419	27%	56%	4%	0.04	0.58	0.05	MLML
CC5	A	N fork-Stemple	38.98531	122.48386	3%	89%	4%	0.04	0.03	0.03	MLML
CC6	A	Stemple-Harley	38.98800	122.48361	25%	60%	2%	0.05	0.04	0.06	MLML
CC7	Surface	Harley-Rocky	38.98440	122.47911	5%	93%	1%	0.55	0.04	0.13	MLML
CC8	A	Harley-Rocky	38.98155	122.47916	12%	70%	18%	0.1	0.07	0.15	MLML
CC8	B	Harley-Rocky	38.98155	122.47916	9%	90%	0.40%	0.18	0.05	0.06	MLML
CC8	C	Harley-Rocky	38.98155	122.47916	2%	97%	1%	0.92	0.07	1.1	MLML
CC9	A	Rocky-Jack	38.97892	122.47556	9%	90%	1%	0.24	0.05	0.04	MLML
CC9	B	Rocky-Jack	38.97892	122.47556	11%	87%	2%	0.07	0.04	0.05	MLML
CC10	A	Rocky-Jack	38.97793	122.47269	9%	88%	3%	0.24	0.06	0.09	MLML
CC10	B	Rocky-Jack	38.97793	122.47269	7%	93%	1%	1.49	0.04	0.06	MLML
CC10	C	Rocky-Jack	38.97793	122.47269	3%	95%	2%	1.68	0.07	0.12	MLML
CC11	A	Rocky-Jack	38.97612	122.46973	18%	80%	2%	0.05	0.06	0.06	MLML
CC11	B	Rocky-Jack	38.97612	122.46973	17%	80%	3%	0.09	0.1	0.22	MLML
CC11	C	Rocky-Jack	38.97612	122.46973	59%	29%	11%	0.23	3.02	0.09	MLML
CC12	A	Jack-Judge	38.97219	122.46763	7%	92%	0.20%	0.24	0.05		MLML
CC12	B	Jack-Judge	38.97219	122.46763	5%	95%	0.50%	1.42	0.07	0.08	MLML

Table B1. (Continued)

Station Code	Replicate	Creek Reach	Latitude	Longitude	Percent of total sample weight			Mercury concentration (ppm)			Mercury Analytical Lab
					Silt	Sand	Gravel	Silt	Sand	Gravel	
CC12	C	Jack-Judge	38.97219	122.46763	10%	85%	5%	0.18	0.08	0.05	MLML
CC13	A	Jack-Judge	38.96725	122.46559	4%	96%		0.63	0.09		MLML
CC13	B	Jack-Judge	38.96725	122.46559	6%	94%		0.07	0.07		MLML
CC13	C	Jack-Judge	38.96725	122.46559	10%	89%		1.52	0.06		MLML
CC14	A	Jack-Judge	38.96289	122.46700	7%	71%	4%	0.45	1.43	0.4	ALS
CC14	B	Jack-Judge	38.96289	122.46700	5%	90%	1%	1.25	0.82	0.71	ALS
CC15	A	Jack-Judge	38.96143	122.46083	5%	88%	2%	0.23	0.66	0.26	ALS
CC15	B	Jack-Judge	38.96143	122.46083	11%	77%	3%	0.5	0.54	0.46	ALS
CC16	A	Brushy-Petrified	38.95848	122.45587	5%	92%	4%	0.09	0.12	0.07	MLML
CC16	B	Brushy-Petrified	38.95848	122.45587	2%	86%	12%	1.97	0.06	0.05	MLML
CC16	C	Brushy-Petrified	38.95848	122.45587	2%	68%	30%	0.6	0.06	0.04	MLML
CC17	A	Petrified-Trout	38.95584	122.45328	6%	70%	25%	0.06	0.07	0.04	MLML
CC17	B	Petrified-Trout	38.95584	122.45328	3%	75%	22%	0.1	0.11	0.1	MLML
CC17	C	Petrified-Trout	38.95584	122.45328	10%	79%	12%	0.1	0.07	0.12	MLML
CC18	A	Trout-Crack	38.94464	122.44292	12%	73%	4%	1.31	1.56	1.77	ALS
CC18	B	Trout-Crack	38.94464	122.44292	15%	81%	3%	2.69	0.4	0.59	ALS
CC18	C	Trout-Crack	38.94464	122.44292	9%	67%	2%	0.75	0.52	0.15	ALS
CC19	A	Trout-Crack	38.94258	122.43896	4%	30%	24%	0.16	0.24	0.27	ALS
CC19	B	Trout-Crack	38.94258	122.43896	14%	73%	10%	1.45	1.16	2.84	ALS
CC19	C	Trout-Crack	38.94258	122.43896	27%	61%	7%	0.33	0.67	0.31	ALS
CC20	A	Trout-Crack	38.94445	122.43497	10%	74%	9%	0.47	1.23	4.75	ALS
CC20	B	Trout-Crack	38.94445	122.43497	13%	77%	6%	1.17	0.23	0.61	ALS
CC20	C	Trout-Crack	38.94445	122.43497	7%	92%	2%	0.52	0.29	0.3	ALS
CC21	A	Trout-Crack	38.94515	122.42945	12%	67%	9%	0.58	0.62	1.2	average
CC22	A	Trout-Crack	38.94516	122.42305	12%	67%	9%	0.58	0.62	1.2	average
CC23	A	Trout-Crack	38.94795	122.41965	16%	80%	4%	0.34	0.74	0.41	ALS
CC23	B	Trout-Crack	38.94795	122.41965	19%	25%	21%	0.49	0.67	0.44	ALS
CC23	C	Trout-Crack	38.94795	122.41965	8%	52%	13%	0.52	0.54	0.68	ALS

Table B1. (Continued)

Station Code	Replicate	Creek Reach	Latitude	Longitude	Percent of total sample weight			Mercury concentration (ppm)			Mercury Analytical Lab
					Silt	Sand	Gravel	Silt	Sand	Gravel	
CC24	A	Trout-Crack	38.94807	122.41814	14%	52%	14%	1.07	1.07	0.54	average
CC25	A	Trout-Crack	38.94541	122.41560	8%	80%	2%	3.58	0.76	0.93	ALS
CC25	B	Trout-Crack	38.94541	122.41560	13%	34%	22%	1.01	3.34	0.46	ALS
CC25	C	Trout-Crack	38.94541	122.41560	23%	40%	21%	0.46	0.34	0.32	ALS
CC26	A	Trout-Crack	38.94266	122.41513	15%	52%	15%	1.68	1.48	0.57	average
CC27	Surface	Crack-Davis	38.94101	122.40026	6%	94%		1.67	0.06		MLML
CC28	A	Crack-Davis	38.93992	122.39310	17%	77%		0.88	0.45		ALS
CC28	B	Crack-Davis	38.93992	122.39310	18%	29%	29%	1.11	0.33	0.29	ALS
CC28	C	Crack-Davis	38.93992	122.39310	5%	84%	12%	0.36	0.46	0.46	ALS
CC29	A	Crack-Davis	38.94395	122.39084	16%	65%	7%	0.25	0.41	0.3	ALS
CC29	B	Crack-Davis	38.94395	122.39084	9%	67%	9%	1.56	0.38	0.41	ALS
CC29	C	Crack-Davis	38.94395	122.39084	26%	49%	12%	0.82	0.42	0.35	ALS
CC30	A	Crack-Davis	38.93959	122.38425	8%	48%	8%	0.68	0.7	0.46	ALS
CC30	B	Crack-Davis	38.93959	122.38425	9%	25%	13%	0.38	0.4	0.29	ALS
CC30	C	Crack-Davis	38.93959	122.38425	2%	26%	14%	1.19	1.11	0.47	ALS
CC31	A	Davis-Bear	38.93426	122.37315	17%	54%	12%	0.39	1.35	1.43	average
CC32	A	Davis-Bear	38.93078	122.37030	8%	90%	1%	0.78	1.75	1.45	ALS
CC32	B	Davis-Bear	38.93078	122.37030	21%	44%	8%	0.23	1.04	1.33	ALS
CC32	C	Davis-Bear	38.93078	122.37030	20%	29%	26%	0.17	1.27	1.5	ALS
CC33	Surface	Davis-Bear	38.92743	122.37019	4%	92%	4%	0.42	0.08	0.06	MLML
CC34	A	Davis-Bear	38.92610	122.37391	6%	63%	15%	0.92	1.27	3.76	ALS
CC34	B	Davis-Bear	38.92610	122.37391	11%	54%	14%	0.49	1.53	2.52	ALS
CC34	C	Davis-Bear	38.92610	122.37391	11%	56%	16%	0.75	2.13	2.05	ALS
CC35	A	Davis-Bear	38.92455	122.37040	6%	93%		0.33	2.16		ALS
CC35	B	Davis-Bear	38.92455	122.37040	26%	71%	4%	0.21	4.56	1.92	ALS
CC35	C	Davis-Bear	38.92455	122.37040	16%	74%	5%	0.27	1.23	1.56	ALS
CC36	A	Davis-Bear	38.92168	122.36372	10%	74%	2%	11.2	1.28	2.21	ALS
CC36	B	Davis-Bear	38.92168	122.36372	19%	66%	4%	0.3	1.18	2	ALS

Table B1. (Continued)

Station Code	Replicate	Creek Reach	Latitude	Longitude	Percent of total sample weight			Mercury concentration (ppm)			Mercury Analytical Lab
					Silt	Sand	Gravel	Silt	Sand	Gravel	
CC36	C	Davis-Bear	38.92168	122.36372	19%	74%	4%	10.05	1.86	0.71	ALS
CC37	A	Davis-Bear	38.92291	122.35700	6%	94%		1.67	0.06		average
CC38	A	Davis-Bear	38.91930	122.35362	13%	55%	15%	0.32	2.2	1.69	ALS
CC39	A	Davis-Bear	38.91754	122.35429	5%	95%	0.30%	0.48	0.06		MLML
CC39	B	Davis-Bear	38.91754	122.35429	4%	95%	1%	2.71	0.06	0.05	MLML
CC39	C	Davis-Bear	38.91754	122.35429	2%	97%	1%	1.01	0.07	11.84	MLML
CC40	A	Davis-Bear	38.91584	122.35121	7%	89%	2%	1.56	1.43	4.08	average
CC41	A	Davis-Bear	38.91845	122.34826	10%	83%	3%	1.73	2.79	4.2	ALS
CC42	A	Davis-Bear	38.92386	122.34142	4%	90%	6%	1.11	9.95	0.06	MLML
CC42	B	Davis-Bear	38.92386	122.34142	13%	56%	32%	0.14	0.09	0.09	MLML
CC42	C	Davis-Bear	38.92386	122.34142	3%	87%	9%	0.19	0.06	0.1	MLML
CC43	A	Davis-Bear	38.92321	122.33832	12%	50%	38%	0.12	0.14	0.11	MLML
CC43	B	Davis-Bear	38.92321	122.33832	7%	69%	24%	0.55	0.1		MLML
CC43	C	Davis-Bear	38.92321	122.33832	5%	66%	29%	0.34	0.13	0.05	MLML
CC44	A	Davis-Bear	38.92597	122.33509	2%	94%	4%	1.93	0.08	0.14	MLML
CC44	B	Davis-Bear	38.92597	122.33509	5%	92%	3%	2.78	0.07	0.32	MLML
CC44	C	Davis-Bear	38.92597	122.33509	15%	72%	13%	0.15	0.09	0.09	MLML
CC45	A	CC Settling Basin	38.68292	121.67314	19%	46%	25%	0.23	0.22	0.25	MLML
CC45	B	CC Settling Basin	38.68708	121.67383	16%	54%	22%	0.34	0.35	0.33	MLML
CC45	C	CC Settling Basin	38.68400	121.67669	19%	55%	19%	0.42	0.32	0.29	MLML
CC45	D	CC Settling Basin	38.67858	121.67325	18%	52%	23%	0.29	0.38	0.39	MLML

Table B2. Mercury concentrations in tributaries to Cache Creek.

Tributary	Sample code	Latitude	Longitude	Watershed area (km^2)	Percent of total sample weight			Mercury concentration (ppm)			Mercury Analytical Lab[2]
					Silt	Sand	Gravel	Silt	Sand	Gravel	
Harley Gulch	HG1	38.98651	-122.47852	13.9	31%	46%		2.56	1.79		ALS
Harley Gulch	HG2	38.98697	-122.47859	13.9	6%	43%		5.12	0.51		ALS
Harley Gulch	HG3	38.98650	-122.47820	13.9	3%	34%		3.24	1.82		ALS
Harley Gulch	HG4	38.98637	-122.47840	13.9	20%	38%		3.11	4.21		ALS
Harley Gulch	HG5	38.98723	-122.47834	13.9	7%	53%		8.47	0.63		ALS
Harley Gulch	HG6	38.98711	-122.47761	13.9	7%	40%		3.5	0.82		ALS
Harley Gulch	HG7	38.98706	-122.47796	13.9	5%	64%		11.1	0.33		ALS
Harley Gulch	HG8	38.98741	-122.47761	13.9	5%	55%		1.57	23.6		ALS
Rocky Creek	RC1	38.97889	-122.47657	38.0	10%	88%	2%	0.13	0.15	0.05	MLML
Rocky Creek	RC2	38.97841	-122.47740	38.0	9%	83%	8%	0.06	0.05	0.60	MLML
Jack Creek	JC1	38.97258	-122.46674	6.3	11%	79%	10%	0.05	0.05	0.04	MLML
Jack Creek	JC2	38.97303	-122.46570	6.3	25%	43%	32%	0.08	0.07	0.07	MLML
Judge Davis Ck	JD1	38.96183	-122.45933	6.4	2%	26%	26%	0.61	0.19	0.13	ALS
Judge Davis Ck	JD2	38.96225	-122.45939	6.4	4%	31%	29%	0.10	0.17	0.42	ALS
Brushy Creek	BR1	38.96072	-122.45642	6.1	2%	16%	24%	0.05	0.24	0.15	ALS
Brushy Creek	BR2	38.96056	-122.45603	6.1	5%	13%	40%	0.03	0.25	0.13	ALS
Petrified Creek	PC1	38.95723	-122.45642	3.5	8%	70%	22%	0.09	0.06	0.08	MLML
Petrified Creek	PC2	38.95657	-122.45788	3.5	8%	72%	21%	0.09	0.08	0.09	MLML
Trout Creek	TC1	38.95021	-122.45384	6.5	3%	75%	22%	0.13	0.17	0.12	MLML
Trout Creek	TC2	38.94950	-122.45463	6.5	2%	72%	26%	0.16	0.11	0.13	MLML
Crack Canyon	CR1	38.94194	-122.40981	9.8	2%	43%	15%	0.18	0.28	0.27	ALS
Crack Canyon	CR2	38.94175	-122.40961	9.8	1%	19%	26%	0.15	0.37	0.40	ALS
Crack Canyon	CR3	38.94175	-122.40975	9.8	2%	36%	40%	0.23	0.56	0.43	ALS
Davis Creek	DC1	38.93061	-122.37800	49.8	2%	67%	22%	0.14	0.44	0.30	ALS
Davis Creek	DC2	38.93050	-122.37811	49.8	3%	50%	30%	1.70	0.46	0.33	ALS
Davis Creek	DC3	38.93044	-122.37819	49.8	3%	56%	20%	0.14	1.61	0.38	ALS

Table B3. Mercury deposits in Cache Creek between the confluence of Harley Gulch and Bear Creek.

Station Code	Creek Reach	Latitude	Longitude	Surface Area (m^2)	Depth (m)	Volume (m^3)	Weight (10^6 kg)	Mercury deposit (kg)
CC7	Harley-Rocky	38.98440	122.47911	7,883	4	31,531	48.2	3.5
CC8	Harley-Rocky	38.98155	122.47916	11,148	4	44,591	68.2	7.7
CC9	Rocky-Jack	38.97892	122.47556	14,541	4	58,165	89.0	4.9
CC10	Rocky-Jack	38.97793	122.47269	12,228	4	48,912	74.8	9.3
CC11	Rocky-Jack	38.97612	122.46973	10,059	4	40,238	61.6	44.0
CC12	Jack-Judge	38.97219	122.46763	6,593	4	26,371	40.3	4.3
CC13	Jack-Judge	38.96725	122.46559	21,128	4	84,512	129.3	15.1
CC14	Jack-Judge	38.96289	122.46700	11,718	4	46,871	71.7	69.6
CC15	Jack-Judge	38.96143	122.46083	16,797	4	67,186	102.8	54.8
CC16	Brushy-Petrified	38.95848	122.45587	4,159	4	16,634	25.5	2.5
CC17	Petrified-Trout	38.95584	122.45328	3,232	4	12,927	19.8	1.7
CC18	Trout-Crack	38.94464	122.44292	10,512	4	42,049	64.3	53.1
CC19	Trout-Crack	38.94258	122.43896	10,608	4	42,431	64.9	40.8
CC20	Trout-Crack	38.94445	122.43497	8,404	4	33,615	51.4	33.5
CC21	Trout-Crack	38.94515	122.42945	4,348	4	17,391	26.6	15.8
CC22	Trout-Crack	38.94516	122.42305	12,121	4	48,486	74.2	44.0
CC23	Trout-Crack	38.94795	122.41965	2,998	6	17,986	27.5	12.9
CC24	Trout-Crack	38.94807	122.41814	18,979	4	75,915	116.1	90.9
CC25	Trout-Crack	38.94541	122.41560	28,634	4.6	131,718	201.5	220.8
CC26	Trout-Crack	38.94266	122.41513	8,518	4	34,073	52.1	57.1
CC27	Crack-Davis	38.94101	122.40026	8,508	4	34,032	52.1	8.5
CC28	Crack-Davis	38.93992	122.39310	6,628	4.6	30,489	46.6	20.6
CC29	Crack-Davis	38.94395	122.39084	10,720	3	32,159	49.2	20.9
CC30	Crack-Davis	38.93959	122.38425	20,683	1.5	31,025	47.5	15.9
CC31	Davis-Bear	38.93426	122.37315	4,416	4	17,664	27.0	26.1
CC32	Davis-Bear	38.93078	122.37030	9,898	3	29,695	45.4	43.9
CC33	Davis-Bear	38.92743	122.37019	7,921	4	31,684	48.5	4.4
CC34	Davis-Bear	38.92610	122.37391	8,267	2	16,535	25.3	36.4
CC35	Davis-Bear	38.92455	122.37040	13,289	4.6	61,129	93.5	207.3
CC36	Davis-Bear	38.92168	122.36372	11,096	4.6	51,041	78.1	175.5
CC37	Davis-Bear	38.92291	122.35681	10,463	4	41,852	64.0	118.4
CC38	Davis-Bear	38.91930	122.35362	9,478	4.6	43,601	66.7	100.4
CC39	Davis-Bear	38.91754	122.35429	11,153	4	44,613	68.3	10.4
CC40	Davis-Bear	38.91584	122.35121	16,685	4	66,739	102.1	148.2
CC41	Davis-Bear	38.91845	122.34826	23,951	4	95,805	146.6	380.6
CC42	Davis-Bear	38.92386	122.34142	5,101	4	20,403	31.2	83.0
CC43	Davis-Bear	38.92321	122.33832	3,317	4	13,267	20.3	2.4
CC44	Davis-Bear	38.92597	122.33509	1,890	4	7,561	11.6	2.3

Table B4. Mercury concentrations in holes dug in Cache Creek.

Station Code	Depth	Percent of total sample weight			Mercury concentration (ppm)			Mercury Analytical Lab
		Silt	Sand	Gravel	Silt	Sand	Gravel	
CC7	Surface	5%	93%	1%	0.55	0.04	0.13	MLML
CC7	1ft	3%	44%	53%	0.12	0.12	0.03	MLML
CC7	2ft	5%	47%	48%	0.14	0.18	0.07	MLML
CC7	3ft	5%	51%	44%	0.30	0.12	0.08	MLML
CC27	Surface	6%	94%		1.67	0.06		MLML
CC27	2ft	1%	43%	57%	0.13	0.08	0.06	MLML
CC27	4ft	1%	39%	60%	0.33	0.11	0.10	MLML
CC27	6ft	1%	25%	73%	0.24	0.09	0.09	MLML
CC33	Surface	4%	92%	4%	0.42	0.08	0.06	MLML
CC33	2ft	1%	20%	78%	2.45	0.44	0.13	MLML
CC33	4ft	1%	90%	8%	0.72	0.09	0.23	MLML
CC33	6ft	3%	36%	61%	0.17	0.11	0.04	MLML
HG1	Surface				2.56	1.79		ALS
HG1	3 ft				0.17	0.26		ALS
HG1	6 ft				1.49	0.93		ALS
HG2	Surface				5.12	0.51		ALS
HG2	3 ft				2.86	0.36		ALS
HG2	6ft				1.43	0.54		ALS
HG3	Surface				3.24	1.82		ALS
HG3	3ft				3.33	0.38		ALS

APPENDIX C

Quality Assurance/Quality Control Program

The program had components to assess both accuracy and precision. Accuracy was measured by analyzing both standard reference material (SRM) and by amending a known amount of mercury into Cache Creek sediment and measuring the percent recovery. Precision was assessed in both the laboratory and field. Laboratory precision was determined from repeated measurements of the same digest while field variability was measured by performing duplicate analysis of additional material from the same sample.

Both MLML and ALS measured the mercury concentration of PACS 2 standard reference material[1]. The certified value of PACS 2 is 3.40±0.2-ppm mercury[2]. Recoveries by MLML were between 3.18 and 4.07 with a mean of 3.45 (n=14, Table C1). In contrast, ALS reported that the concentration of the SRM varied between 56 and >100-ppm. Only MLML amended a known amount of mercury into sediment and measured the percent recovery of the spike. The percent recovery of duplicate spiked samples ranged between 67 and 287 percent with an average recovery of 103 percent (n=28, Table C2). Overall, the results suggest that the accuracy of mercury measurements by MLML is acceptable while those of ALS are questionable. The ALS measurements resulted in a follow up investigation to determine whether their data was usable. The results of that investigation are discussed below.

Measurements of precision by both MLML and ALS were acceptable. The RPD of a second analysis of the same field sample at ALS ranged between 6 and 97 percent with an average of 36 percent (n=8, Table C3). The RPD for the same analysis of precision at MLML ranged between 2 and 175 percent with an average of 30 percent (n=14).

Poor performance by ALS in analyzing the standard reference material does not appear to have compromised the accuracy of the remainder of the ALS measurements. ALS was telephoned by the Regional Board upon receiving the results and asked why they might have performed so poorly. ALS indicated that immediately prior to analyzing the SRMs they had analyzed some other samples for the Regional Board with very high mercury content (>100 ppm) and suspected carryover between the two sets of samples. Regional Board staff requested that ALS return all Cache Creek samples. Staff then sent two more PACS 2 samples to ALS for analysis. ALS reported that the two blind samples contained 2.78 and 2.81-ppm mercury. The results are considered acceptable as the certified value for the SRM is 3.40-ppm. Next, Regional Board staff sent nine ALS samples to MLML and requested that MLML split the samples in half and analyze each for mercury (Table C4). The average RPD of mercury in paired MLML samples was 57 percent while the average RPD of the mean of the two MLML values and the ALS value was 45 percent. The difference was not

[1] National Research Council of Canada, M-12 Montreal Road, Ottawa, Ontario, Canada K1A 0R6
[2] Mean and 95% confidence limits

statistically significant ($P>0.25$, two tailed paired t-test). The results suggest that Cache Creek canyon sediment is not homogenous and the same sample can have considerable variation in mercury content. Also, similar amounts of variation are being measured in the same samples by both MLML and ALS. Next, the average mercury concentration measured by MLML was compared with the original value reported by ALS to determine whether either set of measurements was biased high. Again, the two sets of measurements were not different ($P>0.25$, two tailed paired t-test) suggesting that qualitatively similar results would have been obtained if the analysis had been conducted by either laboratory. So, Regional Board staff accepted the results obtained by ALS for sediment samples collected in Cache Creek. For consistency though, all future samples were submitted to MLML for analysis.

Table C1. Summary of PACS 2 standard reference material measurements. The certified value of PACS 2 is 3.40 ±0.2-ppm mercury.

Sample Collection Date	Measured PAC 2 mercury value (ppm)	Recovery (%)	Laboratory
29 Oct 2003	56.4	-	ALS
29 Oct 2003	>100	-	ALS
29 Oct 2003	>100	-	ALS
26 Mar 2004	3.67	108	MLML
26 Mar 2004	3.53	104	MLML
26 Mar 2004	3.54	104	MLML
20 Dec 2004	3.57	106	MLML
20 Dec 2004	3.38	99	MLML
20 Dec 2004	3.36	99	MLML
20 Dec 2004	3.18	94	MLML
20 Dec 2004	4.13	122	MLML
20 Dec 2004	4.07	120	MLML
20 Dec 2004	3.83	112	MLML
20 Dec 2004	3.83	113	MLML
20 Dec 2004	3.86	113	MLML
20 Dec 2004	3.56	105	MLML
20 Dec 2004	3.75	110	MLML

Table C2. Percent recovery by MLML upon adding a known amount of mercury into Cache Creek sediment.

Date	Background sediment concentration (ppm)	Predicted concentration after Addition (ppm)	Percent Recovery of duplicate amendments
26 Mar 2004	0.22	2.62	104/100
26 Mar 2004	0.03	1.77	86/85
26 Mar 2004	0.02	1.24	97/89
20 Dec 2004	0.07	0.47	121/287
20 Dec 2004	2.78	16.31	100/91
20 Dec 2004	0.24	1.37	93/148
20 Dec 2004	0.07	0.131	67/90
20 Dec 2004	0.21	1.21	92/84
20 Dec 2004	0.10	0.73	122/106
20 Dec 2004	0.09	1.35	113/94
20 Dec 2004	0.04	0.26	114/78
20 Dec 2004	0.09	0.25	85/96
20 Dec 2004	0.60	2.78	80/77
20 Dec 2004	0.31	1.61	78/95

Table C3. Duplicate analysis of field samples to estimate precision.

Date	Replicate 1 (ppm)	Replicate 2 (ppm)	RPD	Laboratory
29 Oct 2003	0.29	0.16	58	ALS
29 Oct 2003	0.64	0.68	6	ALS
29 Oct 2003	0.48	0.55	14	ALS
29 Oct 2003	0.49	0.59	19	ALS
29 Oct 2003	0.75	0.61	21	ALS
29 Oct 2003	1.15	0.40	97	ALS
26-Mar-04	0.24	0.22	4	MLML
26-Mar-04	0.03	0.04	11	MLML
26-Mar-04	0.06	0.07	11	MLML
20 Dec-04	0.24	0.06	124	MLML
20 Dec-04	1.93	3.16	48	MLML
20 Dec-04	3.93	5.26	29	MLML
20 Dec-04	0.09	0.10	2	MLML
20 Dec-04	0.06	0.06	11	MLML
20 Dec-04	0.09	0.08	9	MLML
20 Dec-04	0.07	0.10	32	MLML
20 Dec-04	0.08	1.2	175	MLML
20 Dec-04	0.11	0.09	27	MLML
20 Dec-04	0.15	0.10	37	MLML
20 Dec-04	0.06	0.05	13	MLML

Table C4. Comparison of ALS and MLML mercury results (ppm) for the same Cache Creek sample.

Original ALS value	MLML duplicate 1 value	MLML Duplicate 2 value	Mean MLML value	RPD for MLML (%)	MLML ALS RPD (%)
1.25	1.81	4.32	3.07	63	42
2.69	0.42	0.29	0.36	23	77
1.45	1.36	2.04	1.70	29	8
3.58	0.69	11.22	5.96	167	25
1.56	0.5	1.69	1.10	88	18
11.2	1.16	1.04	1.10	7	82
10.05	1.81	2.48	2.15	22	65
1.25	1.81	4.32	3.07	63	42
2.69	0.42	0.29	0.36	23	77
			mean	**57**	**45**